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$ZnGa_2O_4$ and $ZnGa_2O_4$:N thin films applied as sensors for detection of acetaldehyde in ethanol

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Abstract

Acetaldehyde, a byproduct of fermentation, is a highly toxic contaminant. Therefore, it is important to develop cost-effective, fast-response and portable acetaldehyde sensors to monitor the formation of this contaminant in the process. Herein, we have evaluated the potential use of $ZnGa_2O_4$ and $ZnGa_2O_4$:N (referred as ZnGaON) films as vapor sensors of ethanol containing acetaldehyde. Sensors based on $ZnGa_2O_4$ films were successfully prepared by PLD on Al_2O_3 substrates containing interdigitated Pt electrodes. The nitridation was carried out under NH_3 gas flow at 700 °C, to obtain ZnGaON films. The prepared sensors presented high sensitivity to acetaldehyde, allowing identification of acetaldehyde in ethanol (300 ppm). This acetaldehyde concentration corresponds to the limit established by Brazilian legislation to sugarcane alcoholic beverages (*cachaça*). The ZnGaON sensor should be operated at moderate temperature (450 °C), and response time of 43 s and recovery time of 26 s are quite fast. The results strongly suggest that ZnGaON may be considered a potential candidate for the development of an efficient screening test for a highly sensitive and selective identification of acetaldehyde in beverages, foods, or fuel.

Keywords: $ZnGa_2O_4$, ZnGaON, PLD, Gas Sensors, Acetaldehyde**,** acetaldehyde-containing ethanol

1. Introduction

The development of cost-effective, fast-response and portable sensors for the detection of toxic and dangerous gases is in high demand due to the need to protect the well-being and quality of human health, as well as monitoring environment contamination. One target substance to be monitored is acetaldehyde because it is highly carcinogenic according to the International Agency for Research on Cancer [1]. One important way to acetaldehyde exposure is fermented foods and alcohol consumption since it can be naturally produced during fermentation process [2,3]. Thus, monitoring acetaldehyde in fermented foods and drinks is a point of great interest for food industry.

Gas chromatography (GC) and mass spectrometry (MS) are the reference techniques for acetaldehyde identification [4]. However, these techniques involve specific and expensive instrumentation and long periods of analysis [2–4]. So, the development of low cost, simple and realiable acetaldehyde sensor is considered as an actual alternative for screening tests. In this context, semiconductor sensors can be a quite interesting alternative due to their robustness, long term stability and low cost [5,6].

Semiconductor-based ethanol sensors are numerous in the literature [5,7–14], but very few works dealing with acetaldehyde detection can be found [3,15–19]. For instance, Veríssimo *et al.* [15] determined the acetaldehyde content in ciders using the solid phase micro-extraction followed by detection with an acoustic wave sensor based on a piezoelectric quartz crystal coated with a polyoxometalate salt. Gunasekaran *et al.* [16] prepared ZnO:F thin films and used them as gas sensors for acetaldehyde detection in air. Donato *et al.* [17] developed a sensor based on ZnO deposited on crystal microbalance to detect acetaldehyde in air. In other work, Mani *et al* [3] prepared undoped, and Ni, Co and Cu-doped ZnO nanostructured films by chemical spray pyrolysis technique and employed them as sensors for a variety of gas, including methanol, ethanol, acetone, formaldehyde, acetaldehyde, among others. The authors observed, at room temperature, the highest selectivity for the films towards acetaldehyde with a detection limit of 10 ppm.

Among a variety of semiconductor sensors for gas detection, spinel-based materials have attracted much interest for such applications due to their compositional and structural flexibility, which allow different chemical modifications in order to tune their properties [20–22]. In this context, zinc gallium oxide ($ZnGa_2O_4$) and oxynitride ($ZnGa_2O_4$:N) can offer a great potential alternative to be used in sensing practical devices.

$ZnGa_2O_4$ is a wide band gap semiconductor, with band gap energy between 4.5-5.2 eV and it presents interesting luminescent emission [23]. This oxide is transparent in near-UV region, with a strong blue luminescence under excitation of either ultraviolet light or low-voltage electrons [24,25]. Besides these interesting properties, an advantage that makes $ZnGa_2O_4$ a promising material for the use in electronic devices is its high resistance in aggressive chemical environments and its stability in a wide range of temperature [26]. On the other hand, zinc gallium oxynitride ($ZnGa_2O_4$:N, hereafter referred as ZnGaON) presents high interest for visible-light photocatalytic activity [27–30]. It may also be very interesting for gas sensing applications, as showed by Kerlau *et al* [31], who used screen printed gallium oxynitride thin films and observed an important response in the presence of ethanol, CO and propane.

In this paper, we report the preparation of $ZnGa_2O_4$ and ZnGaON films using the pulsed laser deposition (PLD) technique. The oxynitride films were obtained by nitridation of the PLD-deposited oxide films under NH_3 gas flow at 700°C. Based on different literature studies and on the investigations performed by Mani *et al* concerning oxide sensors for detection of different gases [3], both oxide and oxynitride films were investigated for detection of acetaldehyde-containing ethanol aiming a possible screening test of beverages as, for example, the Brazilian cachaça. Our study provides insights into the preparation of promising gas sensor devices for efficient and sensitive acetaldehyde detection.

1.2 Experimental

1.2.1 Preparation of $ZnGa_2O_4$ and ZnGaON films

For the deposition of thin films using PLD technique, labmade sintered target of $ZnGa_2O_4$ was prepared by the conventional solid-state reaction using stoichiometric amounts of Ga_2O_3 (Strem Chemicals – 99,99%) and ZnO (Alfa Aesar – 98%) as starting chemical materials. The reactants were weighed grinded in an agate mortar for about 25 min, uniaxially pressed at 150 kg cm^{-2} and pellets were calcined at 1100 °C for 12h to obtain $ZnGa_2O_4$[32].

The $ZnGa_2O_4$ target was used to grow thin films by PLD onto screen-printed interdigitated Pt electrodes on polycrystalline Al_2O_3 substrates equipped with a Pt resistance heater printed on the reverse side (Figure 1). Before deposition, alumina substrates with platinum electrodes were cleaned by rinsing with distilled water and isopropanol and dried with a hot air gun. Alumina was chosen as a substrate because it is cheap, stable, tough, besides

presenting high mechanical, thermal and chemical resistance [33]. Considering preliminary studies carried out by our research group, the best conditions for films preparation were determined as: deposition at room temperature for 30 min, laser beam energy of 220 mJ, operating at 5 Hz and oxygen pressure in the deposition chamber regulated at 0.06 mbar. A KrF excimer laser with 248 nm radiation wavelength was used.

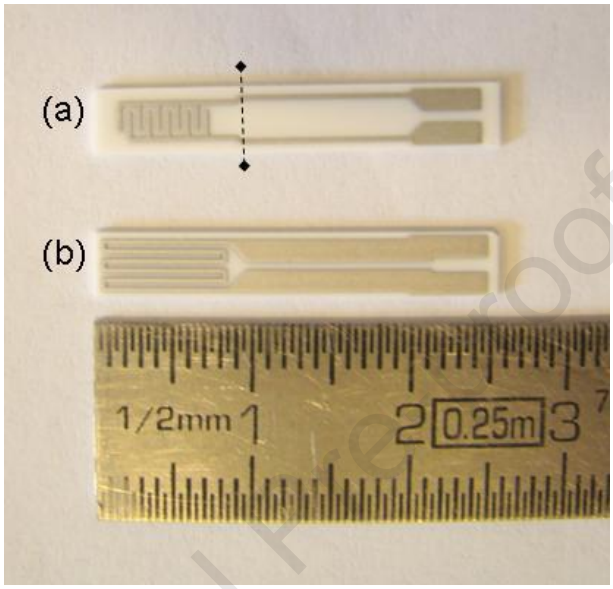

Figure 1 - Al_2O_3 substrate equipped with (a) interdigitated Pt electrodes at one side and (b) Pt heater at the reverse side. Interdigitated area at left of the dashed line.

The preparation of ZnGaON films was carried out by heat treatment under ammonia gas flow of the room temperature PLD-grown $ZnGa_2O_4$ films in a tubular furnace. First, the films were heated, under N_2 flow, up to 400 °C at a heating rate of 10 °C min^{-1}. Then, the N_2 gas was replaced by NH_3 (20 L h^{-1}) and the temperature raised up to 700 °C at a rate of 10 °C min^{-1} [32]. The films remained at this temperature under NH_3 flow for a period of 24 h and then, were inertially cooled. Thin films were also deposited by PLD at 650 °C in order to compare the sensor properties of the crystalline oxide $ZnGa_2O_4$ and the oxynitride.

The films were analyzed by X-Ray diffraction (XRD, Bruker D8 monochromatic $CuK_{\alpha 1}$ radiation) and Scanning Electron Microscopy with Field Emission Gun (FEG-SEM, Jeol 6301-F for imaging).

1.2.2 Sensing Tests

Sensing tests were performed in a teflon testing chamber. Resistance measurements of sensors were simultaneously made by a Picoammeter/Voltage Source (Model 6487 – Keithley,

USA) combined with a scanner (Switch System Model 7001 – Keithley, USA), connected to a computer via an IEEE port. Gas flows were fixed at 6.5 L h^{-1} for pure ethanol, acetaldehyde, and methanol, while a flow at 1.0 L h^{-1} was used for acetaldehyde-containing ethanol sensing experiments. Prior to gas exposure, electrical resistances of the sensors were stabilized under carrier gas (synthetic air for pure ethanol and acetaldehyde tests and synthetic air saturated with ethanol for acetaldehyde-containing ethanol test). After 10 min of exposure to testing gas, the sensors were purged for 20 min using carrier gas flow (synthetic air or synthetic air saturated with ethanol) to allow the sensors to recover. The concentration of acetaldehyde in the mixture with ethanol was 300 mg L^{-1} (300 ppm), with reference to the limit established in the Brazilian legislation for the formulation of sugarcane liquor [34].

Operating temperatures of sensors ranged from 200 to 500 °C [35,36]. Sensor signals defined as R_{gas}/R_0 or R_0/R_{gas} (depending on the reducing/oxidizing character of the atmosphere and sensor signal >1 by convention), where R_0 is the sensor resistance in reference gas (air) and R_{gas} is the sensor resistance under test gas, were used to assess the sensitivity of the sensors. Response time (t_{90}) was determined as the time required for the resistance to fall by 90% and recovery time (t_{90R}) as the time necessary for the resistance to recover 90% of its initial value. Each response consists in an average response of three similar sensors.

1.3 Results and Discussion

1.3.1 Film characteristics

A single-phase spinel-like $ZnGa_2O_4$ labmade target was successfully obtained to prepare the precursor films, as displayed in Figure S1, which shows its XRD pattern. As expected, the films deposited at 650 °C presented the crystalline $ZnGa_2O_4$ phase whereas no peak was observed for the film deposited at room temperature (Figure S2), which is consistent with an amorphous nature. Amorphous films favor the nitridation process, as already described in literature [35–37], that reports a better nitridation performance when the oxide precursor is amorphous or highly disordered. The films, with a thickness of about 500 nm, covered well the grains of the substrate, with good adhesion as well as with quite good electrode substrate coverage even at the $Pt/Al_2O_3/$ interface as shown in Figure 2.

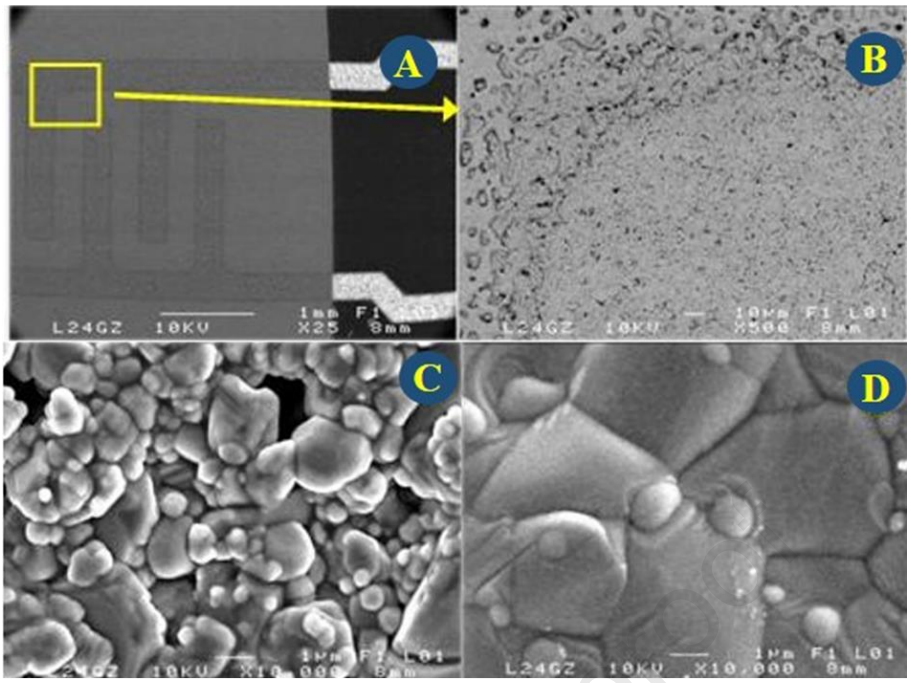

Figure 2 – FE-SEM images of $ZnGa_2O_4$ films grown by PLD, on Pt/alumina substrate electrodes. (A) overview of the film deposited at at 650 ºC and, (B) detail of intermediate region between alumina substrate and Pt electrode; (C) detail of the film covering electrodes and (D) the film in the intermediate region.

The amorphous films were submitted to heat treatment at 700 °C under NH_3 in order to obtain nitrided $ZnGa_2O_4$ (ZnGaON). XRD patterns of films after nitridation (Figure 3A) suggest the formation of an oxynitride poorly crystalline phase by two small peaks at $2\theta = 34.5°$ and 36.8°, which could be related to (006) and (103) crystallographic planes by analogy with GaO_xN_y (ICDD 32-0398), respectively. The nitrided samples exhibited porous and rough aspect, as expected [31,32,38], with quite good substrate coverage even at the Pt/Al_2O_3/ interface. After nitridation, it can be clearly observed on the FE-SEM images the small grains of the films on the large grains of alumina (Figure 3B and 3C). The film presented good adhesion after nitridation (i.e. high enough to enable the sensing measurements), contrary to what de Lucas *et al*. [39] have observed for GaN_xO_y films deposited on GaAs substrates by chemical vapor deposition.

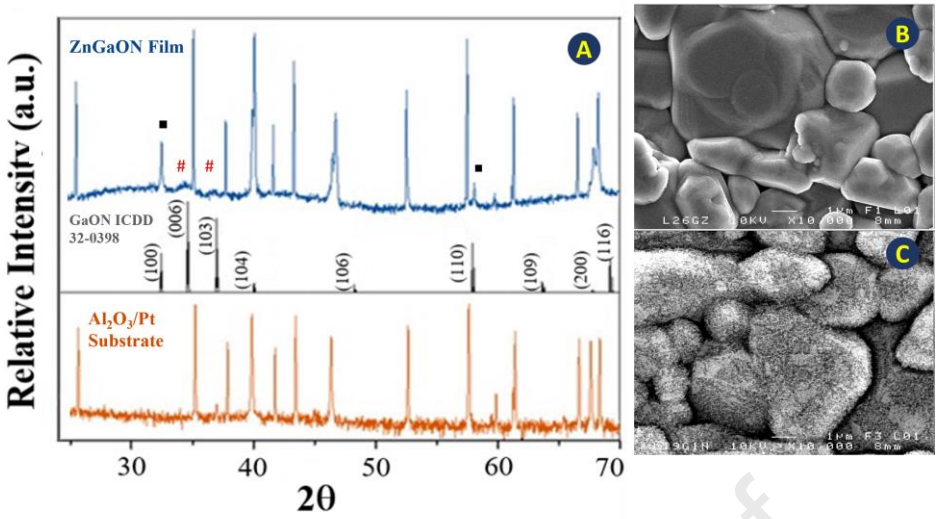

Figure 3 – (A) XRD patterns of the "ZnGaON" film on Pt/alumina. Film grown by PLD at room temperature for 30 min using $ZnGa_2O_4$ target and nitrided at 700 °C for 24 h. #ZnGaON and ▪ unidentified peaks. (B) FE-SEM images of the film deposited at room temperature (amorphous film on alumina grains), (C) FE-SEM images after nitrided at 700 °C.

1.3.2 Gas sensing measurements.

A preliminary study was performed to assess the potential of the sensor towards pure ethanol (Figure S3) and pure acetaldehyde (Figure S4). The first test was carried out exposing sensors to ethanol vapor and the results showed that both crystalline $ZnGa_2O_4$ and ZnGaON films (Figure S3) presented a maximum response at 400 ^oC (sensitivity = 275 and 140 respectively). According to literature, the sensing mechanism in gallate-based sensors results from the presence of ionic defects such as oxygen vacancies or cationic vacancies [20,40]. In the present case, $ZnGa_2O_4$ and ZnGaON presented similar temperatures of maximum sensitivity, with better results for the oxide. Sensitivity values obtained in the present work are smaller than those reported by Kerlau *et al.* [31] using a GaON thick film ($S_{max} \approx 1000$). Moreover, Kerlau *et al.*[31] observed maximum sensitivity at lower temperature (275 °C).

Results for acetaldehyde using both sensors, $ZnGa_2O_4$ and ZnGaON, are displayed in Figure S4 and showed a greater sensitivity to acetaldehyde than to ethanol. The most promising result was observed for ZnGaON, with $S_{max} \sim 11000$ at 400 °C, a remarkable response, which showed ~70-fold increase in maximum sensitivity comparing to ethanol. Ahmadnia-Feyzabad *et al*. [41] also observed a higher response to acetaldehyde than to ethanol using SnO_2-based sensors. The authors attribute this fact to an easier adsorption and decomposition of aldehyde on the surface of the sensor. In relation to sensitivity and selectivity of the sensors, Mani *et al* [3] evaluated the potential employment of undoped ZnO and Ni, Co, and Cu-doped ZnO-based

sensors to detect a variety of gas and confirmed the highest selectivity of the sensors to acetaldehyde at room temperature.

Table 1 lists the acetaldehyde gas sensing performances of the prepared $ZnGa_2O_4$ and ZnGaON based sensors in comparison with different other oxide-based sensors reported in the literature. Concerning recovery time, values of t_{90R} = 1260 s and t_{90} = 143 s for $ZnGa_2O_4$ at 450 °C and t_{90R} = 208 s and t_{90} = 145 s for ZnGaON at 400 °C were observed (Figure S4). According to the preliminary studies, ZnGaON responds faster and recovers even faster to acetaldehyde gas.

Table 1. Comparison of acetaldehyde gas sensing performance of different sensor materials

Sensor	Gas conc. (ppm)	Temp. (°C)	Response (R_0/R_{gas})	Ref
ZnO branched nanorods	100	Room temp.	2.85	[3]
Co-doped ZnO nanorods	100	Room temp.	800	[3]
ZnO microflowers	250	400	8	[8]
In_2O_3 nanospheres	100	300	11	[18]
PdO@ZnO	100	350	76	[19]
Au@SnO_2	500	300	0.85	[42]
Al-doped ZnO	10	500	2250	[43]
ZnO platelets	50	Room temp.	50	[53]
$ZnGa_2O_4$	300	450	1450	
ZnGaON	300	400	11000	This work
ZnGaON	300	450	1130	

As films showed quite high response to acetaldehyde, the ability of differentiating pure ethanol and acetaldehyde-containing ethanol was then investigated (Figure 4). According to the parameters established by Brazilian laws, a limit of 30 mg of acetaldehyde is allowed per 100 mL (300 ppm) of anhydrous ethanol for alcoholic drinks [34]. In Europe, the concentration of acetaldehyde in alcoholic beverages is generally below 500 pm [44]. Maximum sensitivity for acetaldehyde in ethanol was achieved at 450 ^oC (Figure 4B), for both $ZnGa_2O_4$ and ZnGaON. The response time (t_{90}) and recovery time (t_{90R}) were calculated as displayed in Figure 4A.

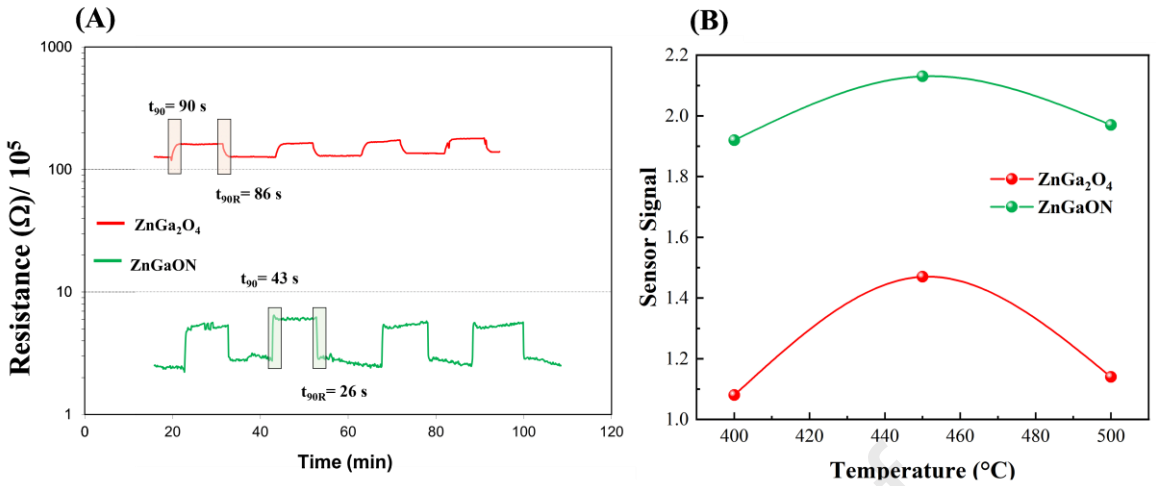

Figure 4 – (A) Time dependent resistance of the $ZnGa_2O_4$ and ZnGaON sensors during exposure to acetaldehyde in ethanol background (300 ppm) at 450 °C; (B) Sensor signals (R_{gas}/R_0) of $ZnGa_2O_4$ and ZnGON sensors towards acetaldehyde exposure in ethanol background as a function of operating temperature.

The oxide and oxynitride sensors showed to be able to identify acetaldehyde in ethanol, however, ZnGaON showed a faster response and recovery time. The faster response observed for ZnGaON has been associated to the greater number of active sites on the surface, since formation of oxynitride typically increases the specific surface area [45–48]. It was also observed that the presence of acetaldehyde in ethanol accelerates the desorption of species from the sensor surface as if alcohol promoted a faster cleaning. This may be associated with the high affinity of ethanol with the surface [7–11,49].

In a previous work of our research group on nitridation of $ZnGa_2O_4$ powders [32], it was observed by EDS analysis that oxide and oxynitride exhibit different amounts of Zn (and consequently different quantity of cation vacancy), indicating that a meaningful loss of Zn upon $ZnGa_2O_4$ nitridation occurred, favored by increasing temperature. It has been stated that, during nitridation, a $ZnGa_2O_4$ spinel phase may undergo phase transformation, being correlated with the lengthening of the Zn-O bonds that favors to bonds breakage and, therefore, loss of Zn cations [50]. Concerning cationic stoichiometry in $ZnGa_2O_4$ materials, Wang *et al* [51] deposited the $ZnGa_2O_4$ films on different substrates and observed that evaluated the Zn/Ga ratio decreases as the temperature of deposition increases above 200 °C due to the higher vapor pressure of Zn in comparison to Ga, being consistent with our previous work [32].

Recently, Chen *et al* [20] prepared formaldehyde sensor based on $CdGa_2O_4$ and $CdGa_2O_4$ decorated CdO nanocrystals and stated that cationic substitution plays an important role on the amount of adsorbed oxygen species on the surface and on the improvement of the

sensing response. As it is known Zn/Ga stoichiometry variation can directly affect sensor sensitivity. Tung *et al* [52] carried out thermodynamic studies of the response of $ZnGa_2O_4$ as a sensor for NO_2 and H_2S gases and observed an increase in sensitivity when the molecules bind to Ga, indicating that the loss of Zn may be associated with the increased sensitivity observed for the sensors studied in this work.

It is important to highlight the possibility of using the same material sensor for detecting different molecules, such as ethanol, methanol, ammonia, acetone, formaldehyde, acetaldehyde, among others. Works in literature also reported the possibility of using gas sensors to detect acetaldehyde in the presence of other interfering gases [15–17,19,53,54]. For instance, Su *et al* [55] prepared sensors based on NiO nanoplates and investigated the performance towards detection of different gases. According to these authors, the NiO sensor is more sensitive to ethanol than any other studied gas, which was attributed to the similar energy between the adsorbed oxygen and the LUMO of ethanol that improve reaction between alcohol molecule and the adsorbed oxygen on the sensor surface.

Concerning the sensitivity, Mani *et al* [3] observed that the sensors were more sensitive to acetaldehyde compared to other gases. In relation to selectivity, the authors evidenced that the Co-doped ZnO sensors showed the highest selectivity towards acetaldehyde detection in the presence of formaldehyde. They stated that, although formaldehyde bond dissociation energy was comparable to acetaldehyde (364 kJ mol^{-1}), a lower response to formaldehyde was obtained due to electron donating effects, where the number of electrons released during the reduction of acetaldehyde is greater than in formaldehyde. Mani *et al.* [3] still emphasized that the sensor sensitivity is dependent on the surface nanostructure morphology. The authors showed that undoped ZnO branched nanorods presented a quicker response and recovery times due to a more open space with loosely packed particle structure. Similar nanostructure characteristics were observed for Co and Cu-doped ZnO samples. Conversely, Ni-doped ZnO sensor exhibited compactly packed nanostructure that may to slow response and recovery times. The authors stated that the morphology and size of the nanostructure determines the degree of electron confinement in the prepared sensors, which is in accordance with Yang *et al.* [56]. In their study, Yang *et al.* [56] stated that gas sensing in semiconductor metal oxides is based on the change of electrical conductivity induced by the gas adsorption/desorption on the surface, and the reactions on surface are strongly dependent on the size, shape, and surface state of sensing materials. Therefore, a sensor with high sensing performance could be obtained by finely tuning the size and shape of the nanoparticles on the material surface [56].

Although the main objective of this work was to prepare $ZnGa_2O_4$ and ZnGaON film-based sensors for acetaldehyde detection in ethanol for applications in alcoholic beverages, response sensitivity studies of the sensors to methanol (Figure S5) and water vapor (Figure S6) were carried out, showing the possibility of applying the prepared sensors for other target molecules. However, our results demonstrated highest sensitivity to acetaldehyde.

Based on all the presented facts, we believe that the stoichiometric imbalance of Zn/Ga together with the presence of oxygen vacancies created by N^{3-} incorporation and the nanostructured grained surface of the $ZnGa_2O_4$:N may be playing a vital role in the highest sensor response in detecting acetaldehyde in ethanol when compared to $ZnGa_2O_4$ sensor. It is still important to highlight that the highest sensitivity of sensors prepared in this work to acetaldehyde is strongly related to its lower bond dissociation energy compared to other gas molecules as suggested by Mani *et al* [3]. In addition, despite being stable at temperatures of 450 ºC as the oxynitride-based sensor (ZnGaON) was prepared at 700 ºC, the sensor was not tested at higher temperatures to avoid thermal surface oxidation. Thus, it is safe for the sensor works at 450 °C to preserve its stability, as a possible thermal oxidation should only effectively occur from 750 °C [5,6].

1.4 Conclusions

ZnGaON films were prepared by nitridation amorphous $ZnGa_2O_4$ previously obtained by PLD at room temperature. Nitridation provided well-adhered films with a continuous porous surface, which is quite suitable for gas sensing application. Crystalline $ZnGa_2O_4$, were also deposited by PLD at 650 °C. Both films, $ZnGa_2O_4$ and ZnGaON, showed to be able to detect acetaldehyde in ethanol vapor (300 mg L^{-1}) and have high potential for use as sensor to acetaldehyde in screening tests. Best results were obtained with the nitrided films, ZnGaON, which showed t_{90} = 43 s and t_{90R} = 26 s, operating at 450 °C. All these results suggest that ZnGaON, and even $ZnGa_2O_4$, may be considered a potential candidate for the development of an efficient screening test for a highly selective and selective identification of acetaldehyde in beverages, foods, or fuel.

1.5 Acknowledgements

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: